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Molecular Transport in Inorganic Membranes: CO_2/CH_4 Separation

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Several large natural gas resources around the world contain large amounts of CO_2. Economic recovery of the CH_4 from streams having CO_2 as the majority component presents numerous technical challenges. One potential separation option is based on inorganic membranes. We describe here general aspects of the CO_2/CH_4 separation process, the technical requirements for a membrane-based separation system, and a summary of the performance characteristics of two inorganic membrane systems (zeolite and amorphous silica). The most promising system relies on a new small-pore, pure SiO_2 zeolite membrane that demonstrates excellent potential for the separation of light gases, especially CO_2/CH_4. The membrane is composed of an array of DDR type zeolite crystals, formed into a layer of typically several microns in thickness on porous alumina tubular supports. The transport properties of numerous gases, with kinetic diameters ranging from 0.26 nm (He) to 0.55 nm (SF_6), suggest a controlling pore size of about 0.35 nm, consistent with the known crystal structure of DDR. Ideal (single-gas derived) selectivities greater than 600 have been observed for CO_2 versus CH_4, demonstrating very low defect levels for membranes with surface areas of greater than 40 cm^2. The highest permeance observed is for CO_2 and the transport of this gas in these DDR membranes is studied in detail. CO_2 permeances are measured over the temperature range 20-100°C and over the differential pressure range of 100 to 2000 kPa. All three membranes studied thus far exhibit CO_2/CH_4 selectivities greater than 100 with little indication of defect-related transport. Thus the observed CO_2 flow can be assigned to "intrinsic" transport through the zeolitic pore structure of DDR. Our approach to modeling this intrinsic (micropore diffusion controlled) single-gas transport is based on the chemical potential gradient driving force and provides a straightforward method for understanding and predicting gas transport behavior as a function of pressure. The model provides an excellent description of the pressure dependence of the CO_2 permeance of DDR membranes over the entire range of conditions studied. The adsorption parameters derived from that analysis are in good agreement with the values derived directly from adsorption isotherms of bulk DDR crystals. Diffusion coefficients derived via this model are in the expected range based on comparisons to zeolites of comparable pore sizes. They are also in good agreement with frequency response measurements on DDR crystals, which will also be reported here. CO_2 adsorption parameters and diffusion coefficients are very similar to those found for amorphous silica membranes. However, H_2O adsorption in DDR membranes is much lower than in silica membranes and the H_2O stability problems found in silica membranes are not present to any measurable degree in DDR membranes.